(12) UK Patent Application (19) GB (11) 2 269 824 (13) A

(43) Date of A Publication 23.02.1994

(21) Application No 9316165.1

(22) Date of Filing 04.08.1993

(30) Priority Data
(31) 4225951 (32) 06.08.1992 (33) DE

(71) Applicant(s)
Leuna-Werke AG

(Incorporated in the Federal Republic of Germany)

Am Haupttor, D-06236 Leuna,
Federal Republic of Germany

(72) Inventor(s)
Uwe Viehweger
Manfred Gebauer
Wolf Kiessling
Horst Stroukal
Rainer Voigt

(51) INT CL[5]
C10L 1/22 1/10

(52) UK CL (Edition M)
C5G GAA GAB G102 G121 G132 G301 G326

(56) Documents Cited
EP 0167358 A

(58) Field of Search
UK CL (Edition L) C5G GAA GAB
INT CL[5] C10L

(74) Agent and/or Address for Service
J B King
Kings Patent Agency Limited, 73 Farringdon Road,
LONDON, EC1M 3JB, United Kingdom

(54) Co-additives for flow improvers

(57) The additives prevent or retard paraffin sedimentation occurring below the turbidity point in petroleum distillates containing flow improvers and lower the temperature of the filterability as well as reduce the tendency of medium distillates to form an emulsion with water.

The additives comprise 25-95% by mass of a solvent mixture consisting of non-polar and weakly polar solvents, the proportion of weakly polar constituent being between 8% and 50%, and 5 - 75% by mass of a nitrogenous constituent which is the product of the reaction at 50° C to 80° C or at 150° C to 180° C of C_{12} -C_{22} fatty amines, having a primary proportion of over 80%, with C_{16} -C_{24} carboxylic acids having at least one double bond, eg oleic and erucic acids; the carboxylic acids being present with a molar surplus of 10% to 30% in relation to the fatty amines.

GB 2 269 824 A

TITLE

Additives for Medium Petroleum Distillates

This invention relates to additives and to a process for the production and use of additives for reducing the limiting temperature of the filterability of medium distillates and for preventing or retarding the settling of the paraffins which separate below the turbidity point, the additives at the same time preventing the formation of emulsions which can occur on intimate contact of the medium distillates provided with additives with water.

The trouble-free storage, transport and use of medium petroleum distillates in the boiling points range 165-400°C, such as diesel fuels, or distillate fuel oils at low temperatures make it necessary to ensure a low solidifying point as well as sufficient flowing and pumping properties up to the regionally varying minimum ambient temperatures to be expected. For Central Europe these are generally assumed to be -21°C, so that for winter diesel fuels a cold filterability temperature of -22°C or lower is usually required. For the trouble-free storage and loading of such petroleum fractions, moreover, the paraffin crystals which separate below the

cloud or turbidity point must be prevented from settling.

In order to obtain a high medium distillate yield and at the same time enable a high final boiling temperature to be adopted the use of additives and of additive packages has become increasingly widespread. It is usual, for example, to add copolymers of ethylene and vinyl acetate of a certain CH_2 sequence and chain length to such distillates, whereby the solidifying point and the limit temperature of the filterability are lowered.

Additives for the retardation or prevention of the settling speed of the paraffin crystals are likewise known, having different effects. DD-AP 253 833, for example, describes an additive based on copolymers of propene and maleic acid anhydride, which at temperatures slightly below the cloud point prevents the separation of paraffin. DE-PS 3049553 describes, in addition to the usual flow improvers, oil-soluble acid amides of polyamines which retard the settling of the paraffin crystals.

EP 0 030 099 describes additive combinations of conventional flow improvers, polar compounds and olefin polymers, which are intended to improve the flow properties of medium oil distillates still further by preventing agglomerations. Finally, DE-OS 4 019 623

describes how additives of primary amines, benzoic acid, formic acid and further constituents completely prevent the settling of the paraffins, even at -22°C and over a period of 336 hours.

With the use of the known additives or additive combinations, however, interference occurs as a result of the formation of emulsion if the medium oils which have received additives are subjected for technological or other reasons to intensive contact with water, the emulsion stability being possibly so high, depending on the composition of the medium oils and the additives, that the intended effect is not obtained or the application properties of the medium oils are made worse.

One object of this invention is to provide additives for the improvement of the low temperature characteristics of paraffinic petroleum distillates, having the additional property of preventing the formation of an emulsion between the medium distillate thus supplemented and water. The invention also provides a process for the manufacture and use of such additives.

This invention seeks to provide additives by which the paraffin sedimentation would be noticeably retarded in petroleum distillates containing flow improvers, the limit temperature of the filterability would be further

reduced and the tendency of supplemented medium distillates to form emulsion with water would be reduced of nullified.

According to this invention there is provided an additive for the improvement of the low temperature properties of petroleum fractions containing n-paraffins and supplemented with cold flow improvers with a polymer base and having a boiling point range of 165 to 400°C and a minimum proportion of 10% by mass (medium distillates) with a boiling point of 330°, for preventing or retarding the sedimentation of paraffin crystals which separate therefrom below the turbidity point and for simultaneously preventing or destabilising emulsions which may form from them with water, wherein the additive comprises 29-95% by mass of a solvent mixture consisting of non-polar and weakly polar solvents, the proportion of weakly polar constituent being between 8% and 35%, and 5-75% by mass of a nitrogenous constituent which is the product of the reaction of fatty amines, having a primary proportion of over 80% and chain lengths of 12 to 22 C atoms, with carboxylic acids having at least one double bond and C- numbers of 17 to 24, the carboxylin acids being present therein with a molar surplus of 10% to 30% in relation to the fatty amines.

Particular advantageous effects are obtained with

such additives wherein the fatty amines largely have 16 and/or 18 C atoms while the carboxylic acids contained therein comprise predominantly oleic acid and/or erucic acid, the solvent mixture containing gas oil fraction or a concentrate of aromatic substances as the non-polar constituent and aliphatic or alicyclic mono-alcohols with a C number of 4 to 8, possibly likewise included as the weakly polar constituent.

The additives according to this invention are preferably produced by a method in which the fatty amines are preliminarily dissolved in a non-polar solvent, such as a concentrate of aromatic substances or a gas oil fraction, and the carboxylic acids in a weakly polar solvent, such as aliphatic or alicyclic alcohols with 4 to 9 C atoms, after which they are intimately mixed at temperatures of either 50-80°C or 150-180°C. It is also possible for the fatty amines and carboxylic acids to be mixed without solvents at temperatures of 150 to 180°C and a solvent mixture of non-polar and weakly polar parts to be added thereto. In this process a weakly polar proportion of 8 to 35% in the total solvent has been found of advantage for the emulsion destabilisation.

It has been found that additives produced with a molar proportion of less that 1 : 1.1 of fatty amines to carboxylic acids, likewise reduce the paraffin

sedimentation below the turbidity point of the medium distillates to which flow improvers have already been added and further improve their cold filterability but that these additives do not have the emulsion destabilising properties of this invention when subjected to the action of water.

On the other hand, additives with molar ratios of over 1 : 1..3 have good de-emulsifying characteristics but do not contribute sufficiently to the improvement of the low temperature properties of the medium oils. A surprising fact is that the fatty amines and carboxylic acids mixed with or without a solvent and in the temperature range 50-18°C have very favourable effects on the reduction of the paraffin sedimentation and cold filterability but that the emulsion destabilisation only takes effect when the production temperature is either between 50 and 80°C or between 150 and 180°C.

The application of additives to medium distillates with cold flow improvers and the application thereto of additives for the retardation of paraffin sedimentation are in practice effected simultaneously. It has thus proved desirable for the additive produced according to this invention to be intimately mixed with a customary flow improver in a further step in which process quantitive ratios between the two components are to be

selected in the light of the purpose in view and the n-paraffin distribution in the medium distillate to which the additive is to be applied. An additive package of this kind can likewise be produced by mixing the dissolved fatty amine and acid constituents with the flow improver in one step.

The additives according to this invention are used by mixing them in accordance with their purpose with medium distillates, which may already contain a flow improver and possibly water, the temperature of the additives being selected to ensure that the flow properties are guaranteed as well as homogeneity, the temperature of the medium distillates being at least 5 degrees above their turbidity point.

The quantity of additive required for the purpose of this invention is related to the boiling characteristics and paraffin distribution of the medium distillate to be given the additive. It has been found suitable for medium distillates already supplemented by flow improver to be provided with additions of 20 to 500 ppm according to the content of constituents having a boiling point of over 330° and according to the amino component contained in the additive. In the event of the addition of a package consisting of the additive according to this invention and a flow improver to a medium distillate

which has receive no additive the concentration to be applied is to be increased in accordance with the mixture ratio, the advantageous additional influence of the additive according to this invention having a favourable effect on the cold flow properties.

This invention is further explained, described and illustrated with reference to the following examples.

In two specimens of medium distillates with the characteristic indicated hereinafter the solid flow and emulsifying characteristics are investigated in accordance with the additives included with flow improver components and additives according to this invention and serving to retard the paraffin sedimentation and to prevent the formation of emulsion with water hereinafter called antisettling/dismulgator.

The emulsification process is investigated in an analogous manner to that prescribed in DIN 51415 (test of the behaviour of aviation fuels when subjected to water). For this purpose 20 ml of aqueous phosphate buffer solution and 80 ml of the medium distillate sample to be examined are shaken in a mixing cylinder for 2 minutes at the rate of 2-3 strokes per second. The mixing cylinder is then placed on a flat vibration-free surface. The contents are evaluated, in stages, after settling but at the latest after they have been left to stand for 5

minutes. The appearance of the (phase) separating layer and also the degree of separation of the two phases are assessed in stages.

The appearance of the separating layer is assessed as follows:

Assessment stage	Appearance of separating layer
1	Clear and clean.
1b	Small clear bubbles not covering more than 50% of the separating layer. No streaks, stripes, suspended particles and/or film on or in the separating layer.
2	Slight streaks, stripes, suspended particles and/or film on or in the separating layer.
3	Moderate streaks, stripes, suspended particles on or in the separating layer and/or slight foam.
4	Dense streaks, stripes, suspended particles on or in the separating layer and/or intense foam.

For the degree of separation the following assessment states are adopted:

Assessment stage	Degree of separation
1	Neither emulsion or sediment nor both in either of the two layers or on the layer of fuel.
2	As in assessment stage 1, but small air bubbles or small drops of water in the layer of fuel.
3	Emulsion or sediment or both in a layer or on the layer of fuel and/or drops in the layer of water or on the wall of the cylinder, except the wall above the layer of fuel.

For the assessment of the cold characteristics the temperature limit value of the filterability (CFPP) is determined according to DIN EN 116 and the settling characteristics of the paraffins observed over a period of 14 days. For this purpose the medium distillate specimen is stored vertically at -22°C in a 250 ml measuring cylinder and the settling of the paraffins observed from a clear phase formation. The slighter the latter, the better the assessment stage by which the effect of the additive is classified.

Characterisation of medium distillates used

Medium distillate	Specimen 1	Specimen 2
Boiling point range, °C	186 - 392	192 - 368
Vol. % above 330°C:	19	12.5
n-paraffin content, % by mass	11.6	14.5
Sulphur content % by mass	0.245	0.088
Density at 20°C, g/cm^3	0.835	0.827
CFPP, °C	-11	-15
Cloud point, °C	- 7	-12

Example 1:

Medium distillate according to Specimen 1 and containing 0.03% by mass of flow improver Leunasol 1000 D (solution of a low molecular weight copolymer of ethylene and vinyl acetate in a hydrocarbon mixture) is given an addition of 0.015% by mass in each case antisettling/dismulgator component, obtained by the reaction, in accordance with this invention and not in accordance with this invention, of fatty amines with a primary part of over 80% and alkyl chain lengths of mainly C_{26} to C_{18} and a carboxylic acid mixture with at least 90% of unsaturated carboxylic acids and an alkyl chain length distribution of at least 83% in the range C_{16} to C_{18} with a minimum proportion of 65% oleic acid, dissolved in a solvent mixture consisting of 75% by mass of medium distillate and 25% by mass of cyclohexanol.

The proportion formed by the solvent in the antisettling/dismulgator component amounts to 55% by mass. For the medium distillate specimens provided with additive and also for a specimen having no additive an assessment is made of the low temperature characteristics and emulsifying characteristics.

	According to this invention	Not according to this invention			Without antisettling/ dismulgator
Molar ratio amine acid	1 : 1.2	1:1	1:1.4	1:2	
Reaction temp. °C	60	60	60	50	
Clear phase, vol%	0	7.3	7.3	7.6	44.2
CFPP, °C	-24	-23	-23	-21	-21
Emulsifying characteristics					
Separating layer	1	2	2	2	1
Degree of separation	2	2	2	2	2

Example 2

Medium distillate in accordance with Specimen 1, with an addition of 0.03% by mass of flow improver Leunasol 1000 D is given an addition of antisettling/ dismulgator components in accordance with Example 1. The reaction temperature selected was 160° C and the

molar ratios set at 1 : 1 and 1 : 1.2 respectively. The low temperature characteristics and emulsifying characteristics were assessed.

	According to this invention	Not according to this invention
Molar ratio amine/acid	1 : 1.2	1 : 1
Reaction temperature, °C	160	160
Clear phase, vol%	0	5.9
CFPP, °C	-22	-22
Emulsifying characteristics		
Separating layer	1	3
Degree of separation	2	2

Example 3

Medium distillate specimens according to Specimen 1 are given an addition, in accordance with Examples 1 and 2, of flow improver and antisettling/dismulgator constituents. The antisettling/dismulgator constituents differ in the molar ratio selected between amine and acid and also in the reaction temperature. The low temperature characteristics and settling or emulsifying characteristics are assessed.

	According to this invention	Not according to this invention			
Molar ratio amine/acid	1 : 1.2	1:1	1:1.2	1:1.4	1:2
Reaction temperature, °C	60	110	110	110	120
Clear phase, vol%	0	0	0	0	59
CFPP, °C	-24	-23	-23	-22	-21
Emulsifying characteristics					
Separating layer	1	3	3	3	3
Degree of separation	2	3	2	2	2

Example 4

Medium distillates in accordance with Specimen 1, supplemented with 0.03% by mass of flow improver Leunasol 1000 D and 0.0115% by mass of antisettling/dismulgator component, obtained by allowing fatty amines with a primary portion of over 80% and alkyl chain lengths of mainly C_{15} to C_{18} to react with erucic acid dissolved in a solvent mixture of 50% by mass of medium distillate and 50% by mass of cyclohexanol, the proportion of solvent being 55% by mass, are examined for their low temperature characteristics and emulsifying characteristics.

	According to this invention	Not according to this invention
Molar ratio amine/acid	1 : 1.2	1 : 1.2
Reaction temperature, °C	60	110
Clear phase, vol%	0	5.8
CFPP, °C	-24	-23
Emulsifying characteristics		
Separating layer	2	3
Degree of separation	2	3

Example 5

Medium distillate according to Specimen 1 is in each case given an addition of 0.03% by mass of flow improver Leunasol 1000 D and 0.03% by mass of antisettling/dismulgator component, produced as described in Examples 1 to 3. The low temperature characteristics and emulsifying characteristics are assessed.

	According to this invention	Not according to this invention	
Molar ratio amine/acid	1 : 1.2	1 : 1	1 : 1.4
Reaction temperature, °C	60	60	60
Clear phase, vol%	0	0	0
CFPP, °C	-24	-23	-23
Emulsifying characteristics			
Separating layer	2	4	4
Degree of separation	2	3	3

Example 6

Medium distillate according to Specimen 2 is given an addition of flow improver Leunasol 1000 D and antisettling/dismulgator component in concentrations of 0.03 to 0.015% by mass, the cold characteristics and emulsifying characteristics then being determined.

The solvent of the antisettling/dismulgator component produced in accordance with Example 1 contains 75% of medium distillate and also 25% of 2-ethyl hexanol, the proportion of solvent in the antisettling/dismulgator component being 55% by mass.

	According to this invention	Not according to this invention	Without antisettling/ dismulgator
Molar ratio amine/acid	1 : 1.2	1 : 1.4	
Reaction temp. °C	60	60	
Clear phase, vol%	20	28	50
CFPP, °C	-29	-29	-29
Emulsifying characteristics			
Separating layer	1b	2	1b
Degree of separation	2	2	2

Example 7

Medium distillate according to Specimen 1 is supplemented in each case with 0.03% by mass of flow improver Leunasol 1000 D and 0.3% by mass of antisettling component (45% by mass of active substance, 55% by mass of solvent mixture of medium distillate and cyclohexanol in a proportion of 3:1).

The low temperature characteristics and emulsifying characteristics are assessed.

Acid used	According to this invention	Not according to this invention*	
	Unsaturated C_{17}-C_{24} acids	Formic acid/ benzoic acid, molar ratio 1.85 : 1	Palimatic acid/ benzoic acid, molar ratio 1.7 : 1
Molar ratio amine/acid	1 : 1.2	1 : 1.2	1 : 1.2
Reaction temp. °C	60	60	60
Clear phase, vol%	0	0	0
CFPP, °C	-24	-23	-24
Emulsifying characteristics			
Separating layer	2	4	4
Degree of separation	2	3	3

*In accordance with German Patent 40 19 623 A 1.

Example 8

Medium distillate according to Specimen 1 is supplemented with 0.03% by mass of flow improver Leunasol 1000 D and 0.015% by mass of antisettling/dismulgator component, obtained by reaction, according to this invention, from fatty amines having a primary proportion of over 80% and alkyl chain lengths of mainly C_{16} to C_{18}, and a carboxylic acid mixture having at least 90% of unsaturated carboxylic acids and an alkyl chain length

distribution of at least 90% in the range C_{16} to C_{22}, with a minimum proportion of 50% of erucic acid, dissolved in a solvent mixture in accordance with Example 1, the proportion of solvent in the antisettling/dismulgator constituent being 55% by mass. The low temperature characteristics and emulsifying characteristics are assessed.

	According to this invention	Not according to this invention	
Molar ratio amine/acid	1 : 1.2	1 : 1	1 : 1.4
Reaction temperature, °C	60	60	60
Clear phase, vol%	0	7.3	7.3
CFPP, °C	-24	-23	-23
Emulsifying characteristics			
Separating layer	1	2	2
Degree of separation	2	2	2

Example 9

0.03% by mass of medium distillate flow improver containing Leunasol 1000 D, in accordance with Example 1, given an addition of 0.015% by mass of antisettling/dismulgator component, obtained by reaction, in accordance with this invention, of fatty amines having a primary proportion of 80% and an alkyl chain length of

mainly C_{16} to C_{18} and a carboxylic acid mixture with at least 90% of unsaturated carboxylic acids and an alkyl chain length distribution of at least 83% in the range C_{16} to C_{18}, with a minimum proportion of 65% of oleic acid, first by direct reaction of the amine and acid constituent at 160°C, followed by the dissolution of the reaction product in a solvent mixture consisting of 75% medium distillate and 25% of cyclohexanol. The proportion of solvent amounts to 55% by mass. The low temperature characteristics and emulsifying characteristics of the medium distillate samples provided with the additive are assessed.

	According to this invention		Not according to this invention
	Reaction followed by addition of solvent	Reaction in solution	
Molar ratio amine/acid	1 : 1.2	1 : 1.2	1 : 1
Reaction temperature, °C	160	160	160
Clear phase, vol%	0	0	5.9
CFPP, °C	-22	-22	-22
Emulsifying characteristics			
Separating layer	1	1	3
Degree of separation	2	1	2

CLAIMS

1. Additive for improving of the low temperature properties of petroleum fractions containing n-paraffins and supplemented with cold flow improvers with a polymer base and having a boiling point range of 165 to 400°C and a minimum proportion of 10% by mass (medium distillates) with a boiling point of 330°, for preventing or retarding the sedimentation of paraffin crystals which separate therefrom below the turbidity point and for simultaneously preventing or destabilising emulsions which may form from them with water, wherein the additive comprises 29-95% by mass of a solvent mixture consisting of non-polar and weakly polar solvents, the proportion of weakly polar constituent being between 8% and 35%, and 5-75% by mass of a nitrogenous constituent which is the product of the reaction of fatty amines, having a primary proportion of over 80% and chain lengths of 12 to 22 C atoms, with carboxylic acids having at least one double bond and C- numbers of 17 to 24, the carboxylin acids being present therein with a molar surplus of 10% to 30% in relation to the fatty amines.

2. Additives in accordance with Claim 1, wherein the fatty amines present mainly have 16 and/or 18 C atoms

while the carboxylic acids contained therein comprise predominantly oleic acid and/or erucic acid, the solvent mixture containing a gas oil fraction or a concentrate or aromatic substances as the non-polar constituent and aliphatic or alicyclic mono-alcohols with a C number of 4 to 8, preferably as weakly polar constituent.

3. Process for the production of an additive in accordance with Claim 1 or 2, in which process a fatty amide mixture, dissolved in a non-polar solvent, is intimately mixed with said carboxylic acids dissolved in a weakly polar solvent, in a molar ratio of 1.1 to 1.3, at temperatures of 50 to 80°C, or at temperatures of 150 to 180°C, until homogeneity is obtained.

4. Process for the production of an additive in accordance with Claims 1 or 2, in which process fatty amines and said carboxylic acids are mixed in a molar ratio of 1.1 to 1.3, first without solvent at temperatures of 150 to 180°C, after which a solvent mixture of non-polar and weakly polar parts is added thereto and the entire resultant substance intimately mixed until homogeneity is reached.

5. Process in accordance with Claims 3 or 4, wherein

the non-polar solvent comprises a gas oil fraction or a concentrate of aromatic substances while the weakly polar solvent comprises aliphatic or alicyclic mono-alcohols with C numbers of 4 to 8, preferably also mixed, the proportion of the weakly polar constituents in the solvent amounting to between 8 and 35%.

6. The use of additives according to any one of Claims 1 to 5, wherein and in relation to those parts of the medium distillate receiving the additives which have a boiling point of over 330°C and to the amine component used, said additives are added in concentrations of 20 to 500 ppm to the medium distillates which contain flow improver and which may contain undissolved water, the temperature of the additives being at least high enough to ensure that they are capable of flowing and homogeneously dispersed, the temperature of the medium distillate being at least 5 degrees above that at which the separation of paraffin commences.

7. Additives for improving the low temperature properties of petroleum fractions, substantially as described herein and exemplified.

8. Process for the production of additives

substantially as described herein and exemplified.

9. Petroleum products containing additives according to, or made by the process of, any preceding claim.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number
GB 9316165.1

Relevant Technical fields

(i) UK Cl (Edition L) C5G (GAA,GAB)

(ii) Int Cl (Edition 5) C10L

Search Examiner
R J WALKER

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search
15 SEPTEMBER 1993

Documents considered relevant following a search in respect of claims 1 - 9

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
:A	EP 0167358 A (E I DU PONT DE NEMOURS AND COMPANY) - see eg abstract	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).